NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Prepared for CARB Co-Processing Working Group
Sacramento, CA | December 13, 2016

Analysis for co-processing fast pyrolysis oil with VGO in FCC units for second generation fuel production

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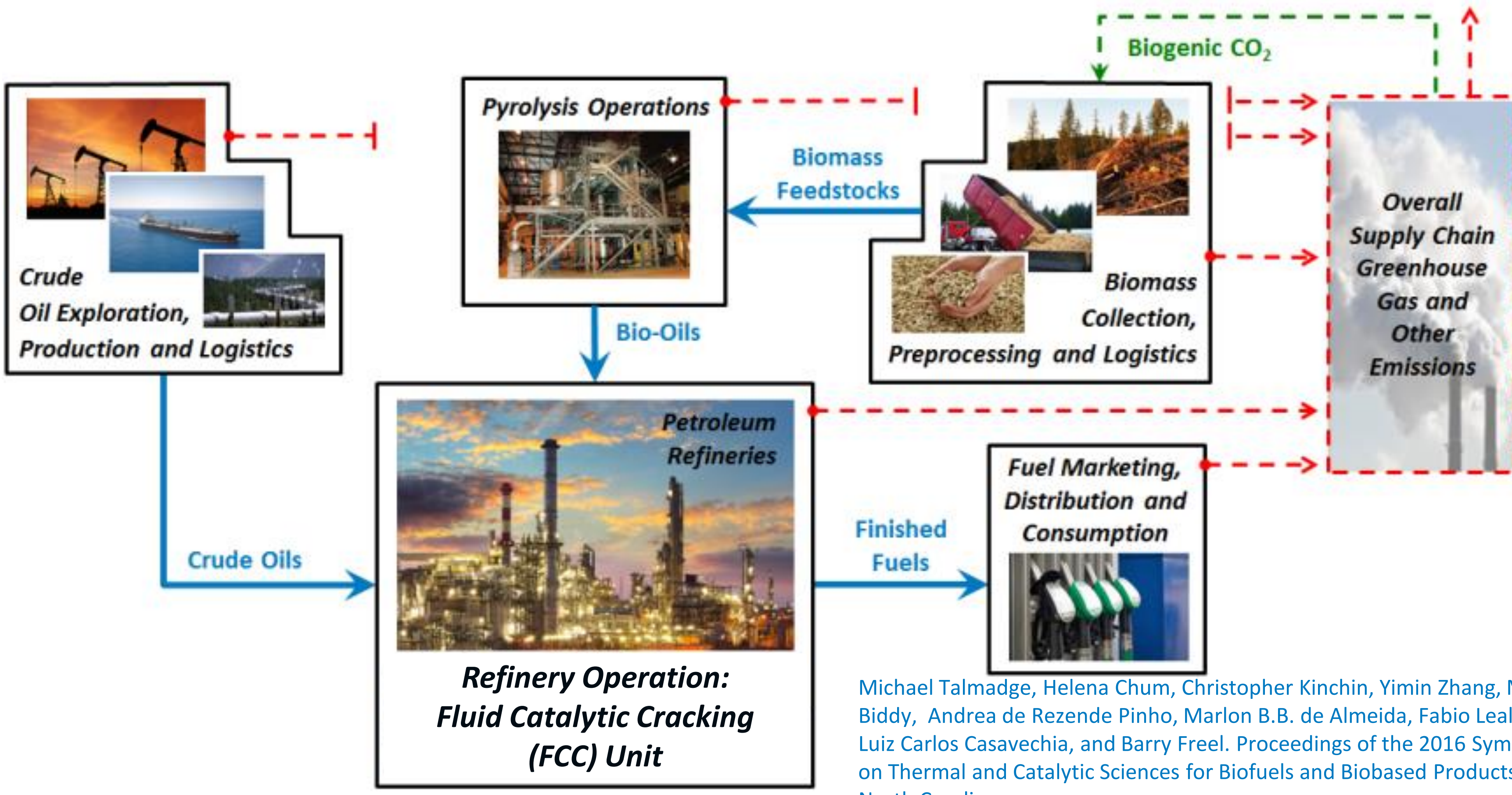
Key Points

Mass balance procedures are accurate, reliable and appropriate to determine renewable gasoline and diesel yields attributable to the addition of biomass pyrolysis oils in FCC co-processing operations, particularly for bio-oil addition under 10%.

^{14}C is not an accurate or reliable method to determine renewable gasoline and diesel yields attributable to the addition of bio-oil in FCC co-processing under 10%

Objective and Overview

Assess the technical and economic feasibility of co-processing raw, pine-derived pyrolysis oil with fossil feedstocks in FCC operation to produce renewable hydrocarbon fuels.



Michael Talmadge, Helena Chum, Christopher Kinchin, Yimin Zhang, Mary Biddy, Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, and Barry Freel. Proceedings of the 2016 Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Raleigh, North Carolina

Fluid Catalytic Cracking (FCC) Unit

PFD Source: CEP, May 2014

FCC Conversion = 100 – LCO – Bottoms

U.S. FCC Capacity

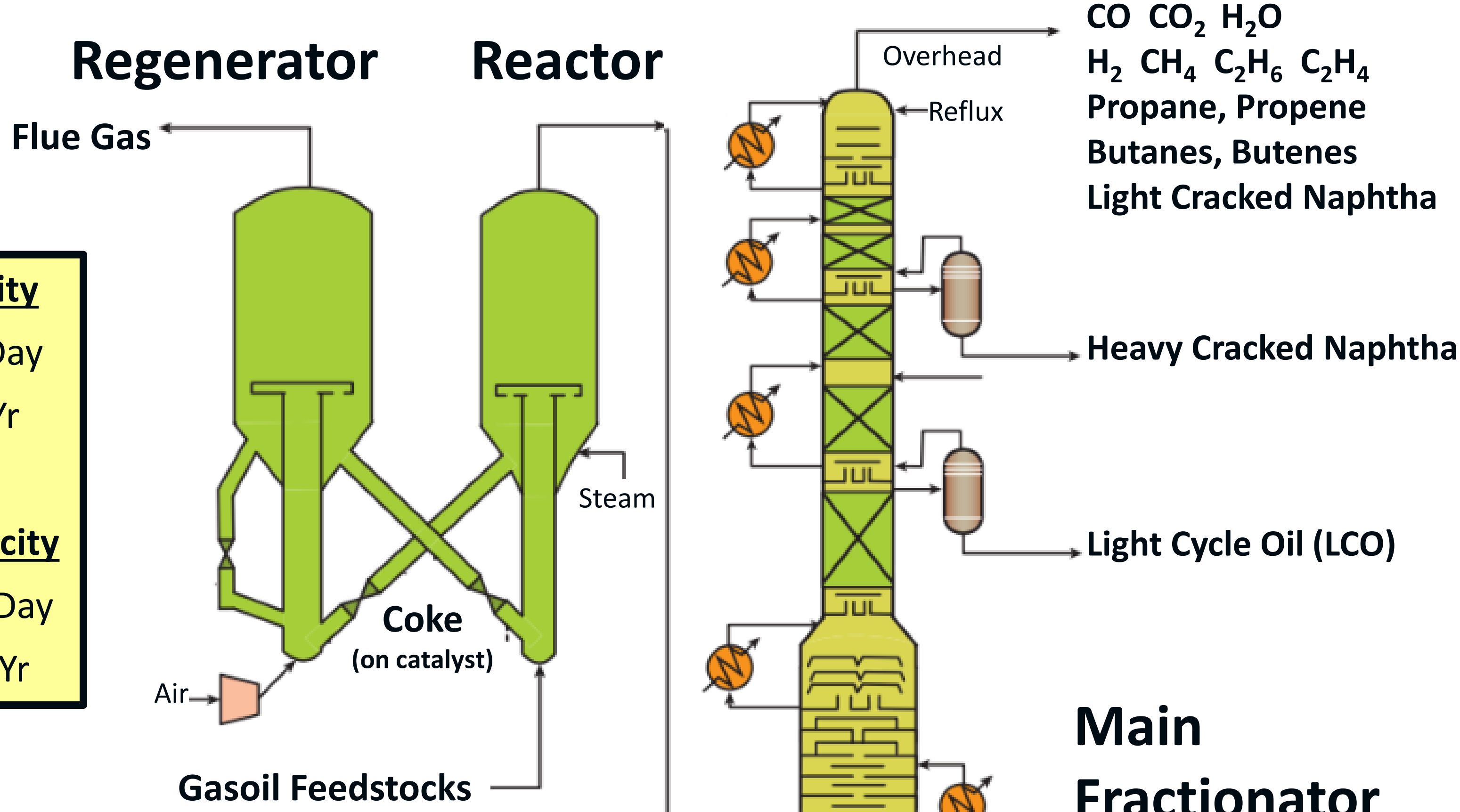
6 MM Barrels/Day

92 B Gallons/Yr

Global FCC Capacity

15 MM Barrels/Day

220 B Gallons/Yr



Petrobras Vacuum Gas Oil (VGO)	
Specific Gravity	0.94
SimDist 10% Boiling Pt.	630 F
SimDist 90% Boiling Pt.	1,050 F

NREL-Petrobras CRADA Information. Do not cite or distribute.

Scope of Py-Oil FCC Co-Processing Analysis

Petrobras "SIX" data for co-processing bio-oil with VGO from crude oil

Feedstock, intermediate and product pricing basis as a function of crude benchmark price

OPIS an IHS Markit company

Capital and operating cost basis for FCC co-processing

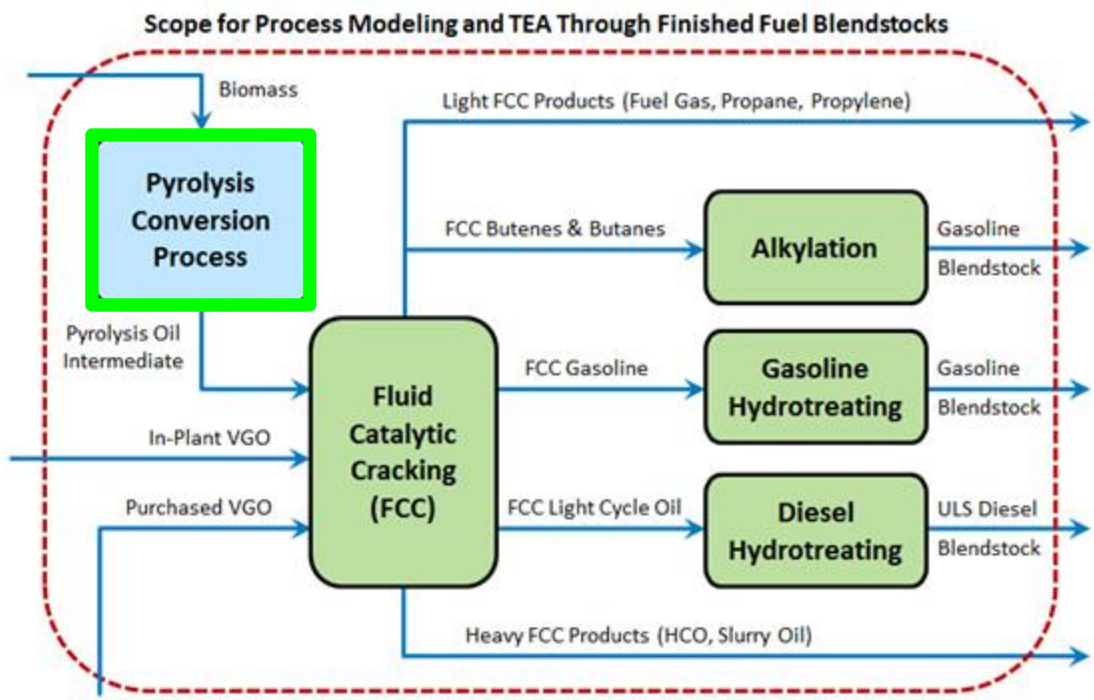
Models developed from Petrobras "SIX" data for FCC operations

aspentech Aspen HYSYS

jmp

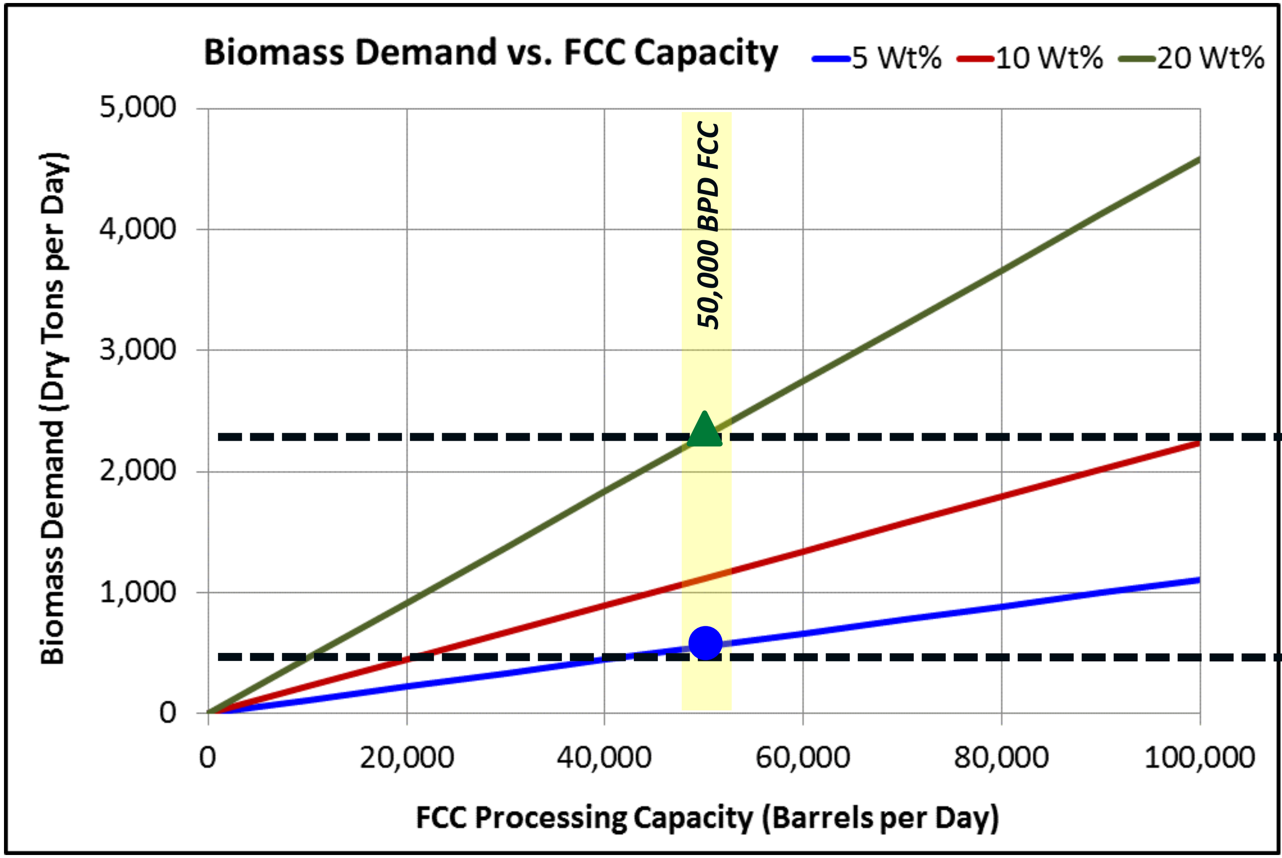
Models for hydrotreating and alkylation based on literature

Modeling and TEA for Pyrolysis Oil Co-Processing Scenarios



Raw Pyrolysis Oil Production TEA

Minimum Selling Price Ranges for Raw Pyrolysis Oil (Feedstock Cost for FCC Co-Processing Analysis)	400 Dry Tonnes / Day	2,000 Dry Tonnes / Day
	$2.00 – $2.10 / Gallon ($84 – $88 / Barrel)	$1.20 – $1.42 / Gallon ($50 – $60 / Barrel)



FCC unit capacity for analysis is 50,000 Bbl / Day

2,000 DMTPD Biorefinery Feeds FCC at ~20 Wt%

400 DMTPD Biorefinery Feeds FCC at ~5Wt%

- *TEA parameters are consistent with those applied for BETO-funded analysis per MYPP.*
- *Capital and operating costs estimated based on PNNL 2013 Fast Pyrolysis Design Report (Report No. PNNL-23053) from Jones et al .*
- *Raw, filtered and stabilized pyrolysis oil with oxygen content of ~50 Wt%, specific gravity of 1.2, moisture content of 25% with organic yield of 60 wt%.*

Experimental Py-Oil Co-Processing Data

Petrobras "SIX" demo unit has same hardware as a commercial FCC

- Feed nozzles
- Riser cyclone
- Packed stripper
- Heat balanced
- Mass flowrate: 200 kg/h
- Riser: L=18 m, d= 2"

Co-Processing Experiments

- Two pine-derived pyrolysis oils with consistent physical properties
- Mass balance range of 96 – 100%
- 3-hour test runs
- Cumulative time w/ py-oil > 400 hours
- Up to 20 wt% pyrolysis oil in FCC feed
- 54 experimental data points

Fuel Processing Technology 131 (2015) 159-166

Co-processing raw bio-oil and gasoil in an FCC Unit

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Fuel 188 (2017) 462-473

Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production

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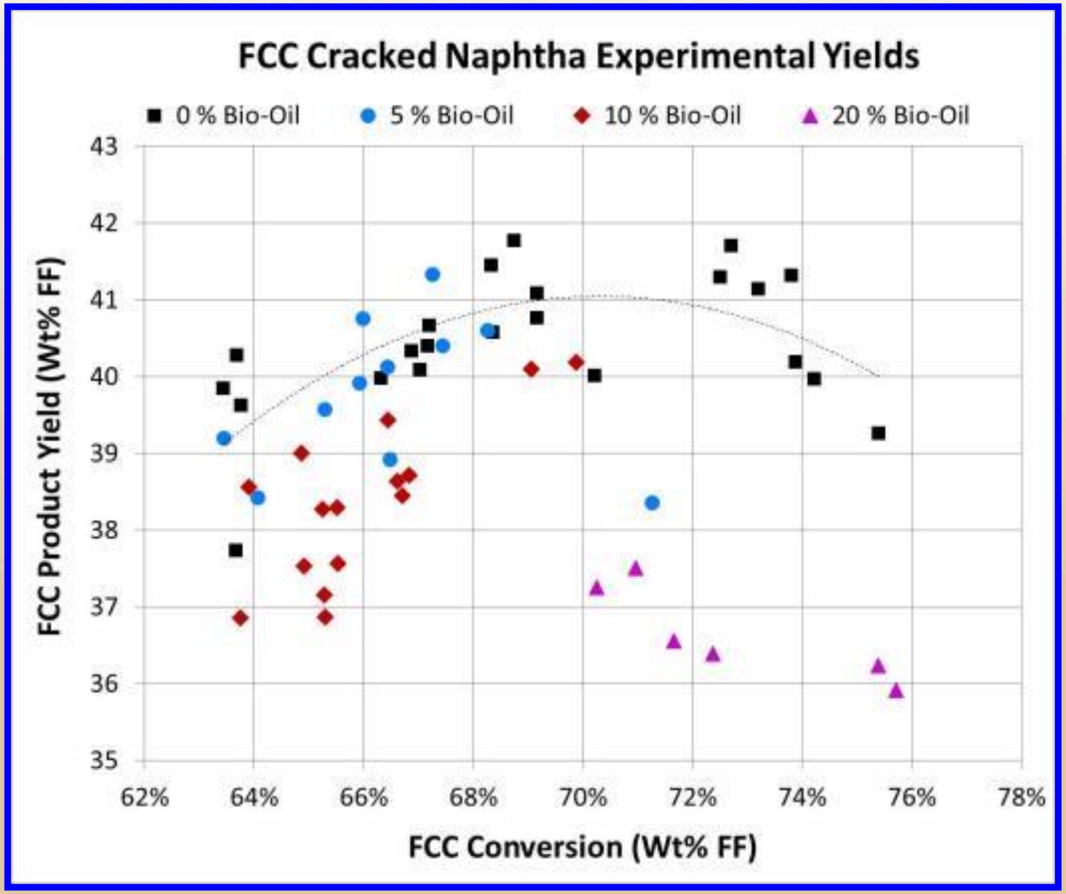
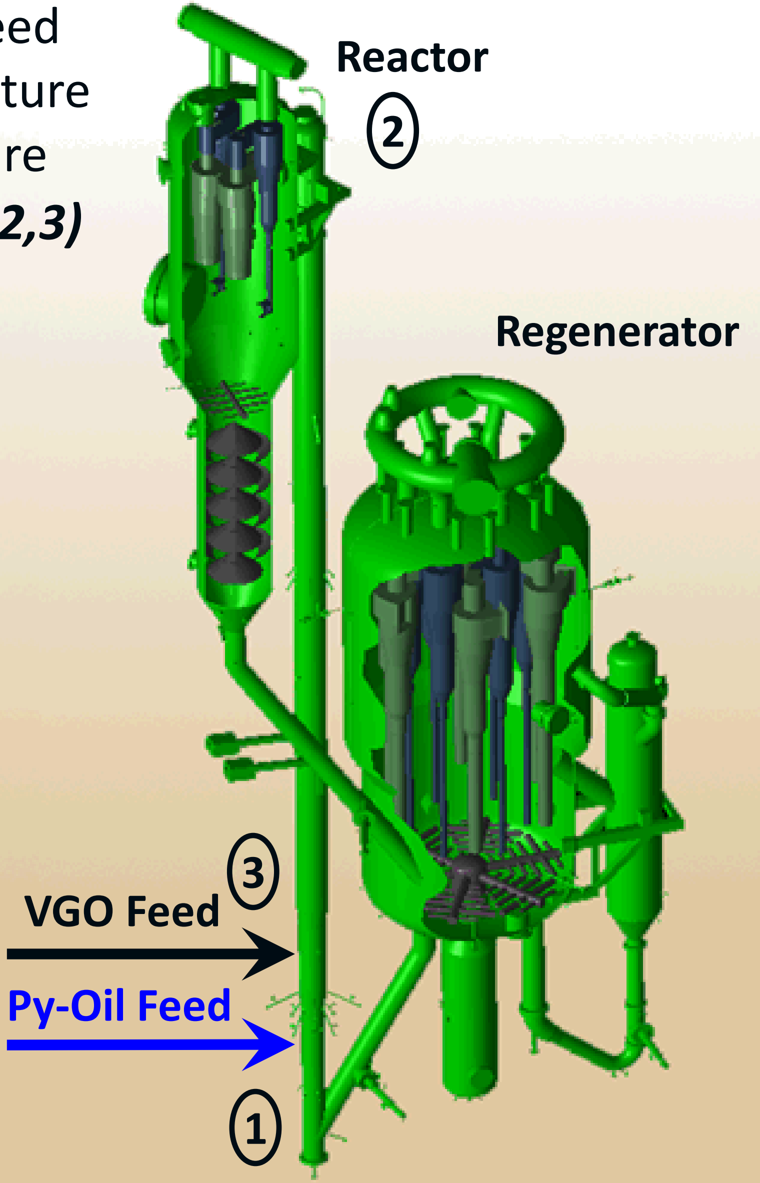
Experimental Py-Oil Co-Processing Data

Experimental Variables:

1. Pyrolysis oil in FCC feed
2. FCC reactor temperature
3. VGO feed temperature

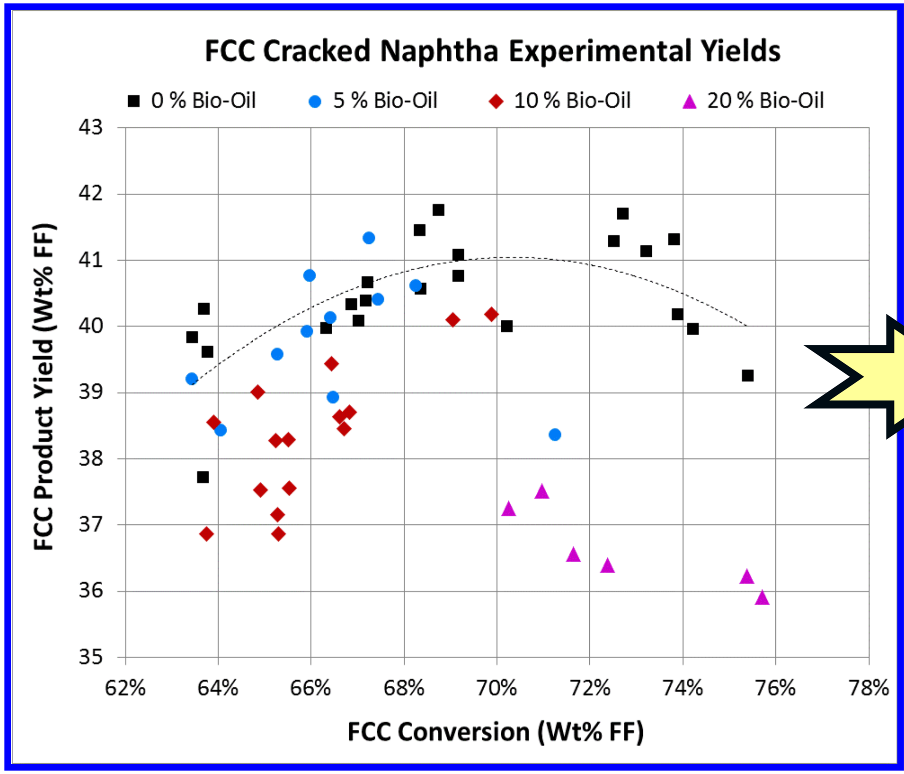
FCC Conversion = f (1,2,3)

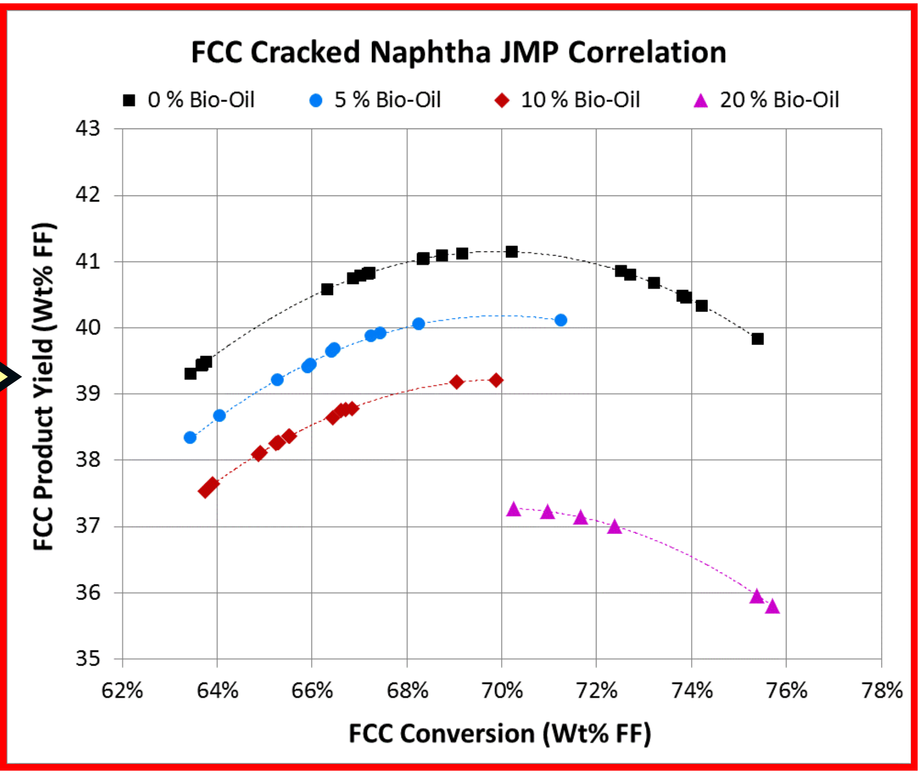




Experimental Py-Oil Co-Processing Data

JMP Software for correlation development





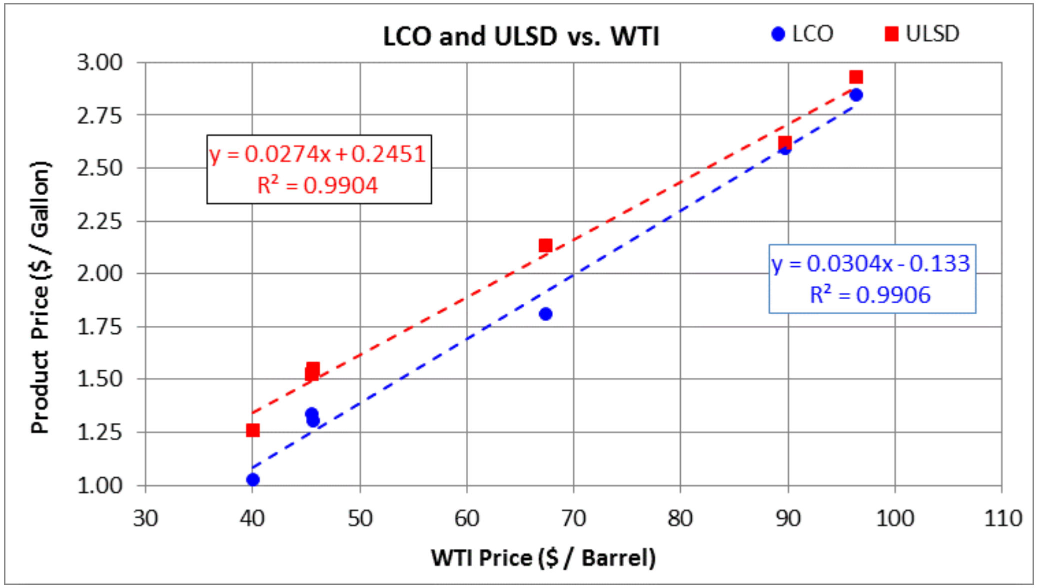
Correlations in FCC Yield Model	Oxygen Species	Refinery Fuels	LPG Products	Liquid Products
	CO CO_2 Water	Dry Gas (C_2-)	Propane Propylene	Cracked Naphtha
		Coke	i-Butane n-Butane	Light Cycle Oil (LCO)
			Butenes	Bottoms Fuel Oil

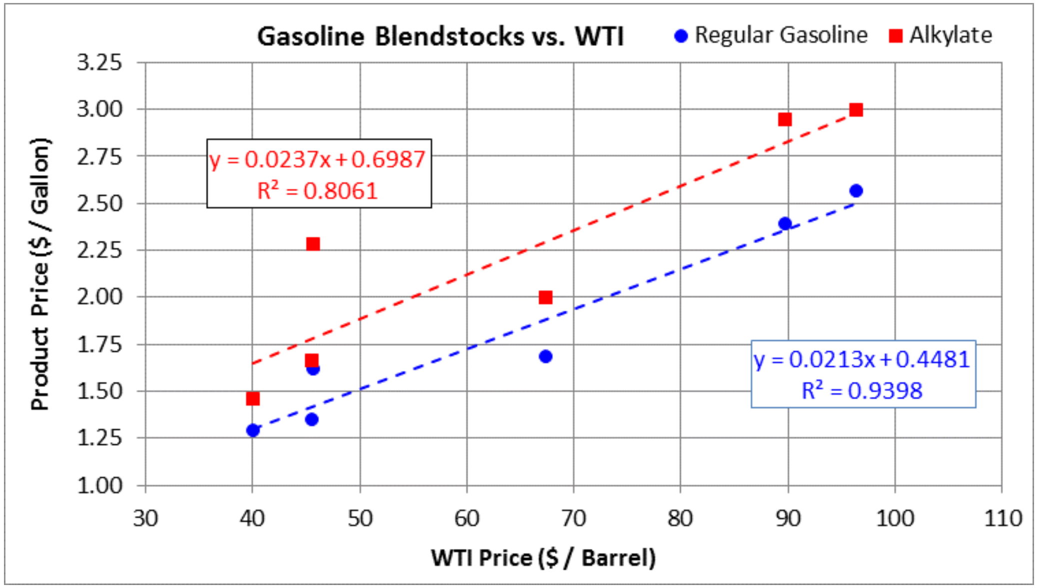
Petroleum Feed and Product Pricing Basis

Feed and product prices for TEA vary with crude oil price

- West Texas Intermediate (WTI) benchmark
- Feed and product prices are functions of WTI price
- Basis for values of Octane and Cetane
- Enables TEA across range of $40 to $100 / barrel

Source of Pricing Data: OPIS International Feedstocks Intelligence Reports (http://www.opisnet.com)

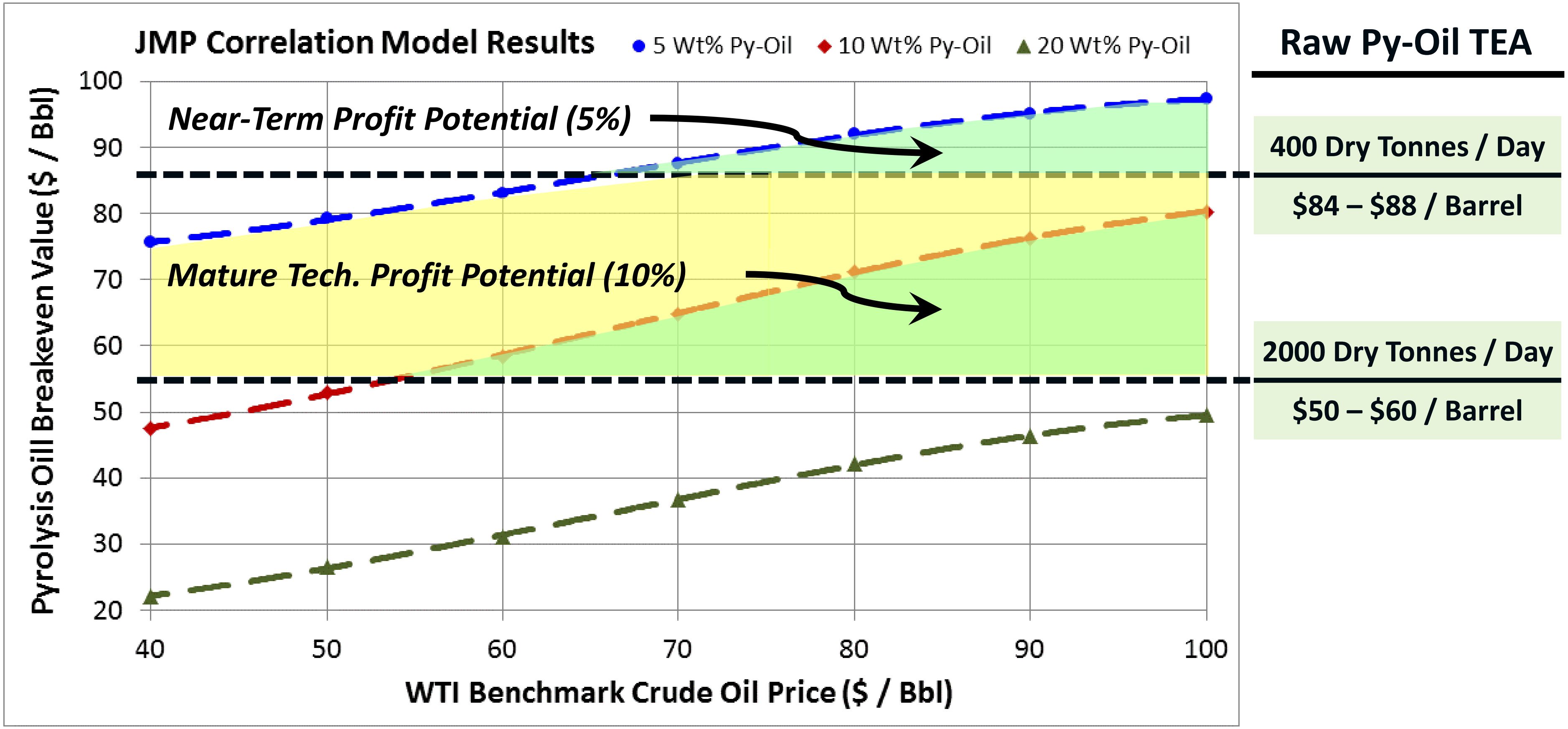




TEA Results – Pyrolysis Oil Breakeven Value

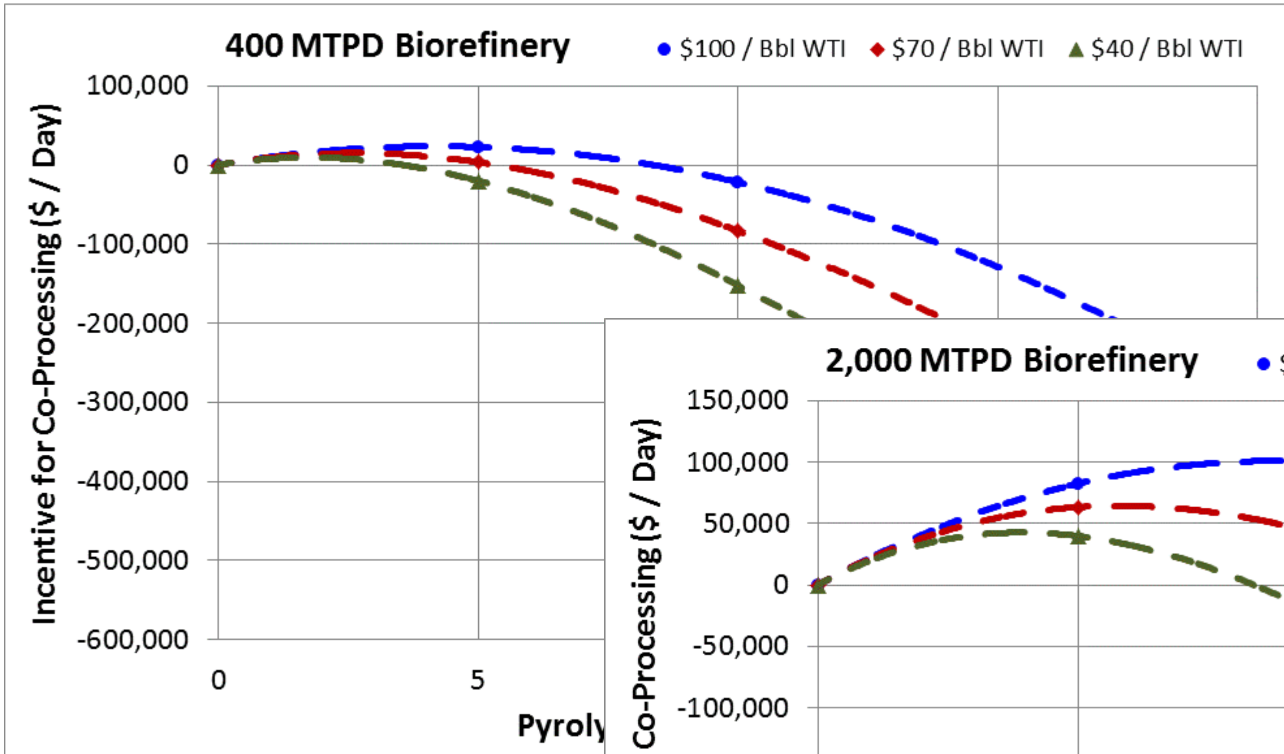
Breakeven Analysis

- Revenue equals cost at the "Breakeven Point"
- "Pyrolysis Oil Breakeven Value" = f (value of products)
- Profit can be realized when cost < "Breakeven Value"

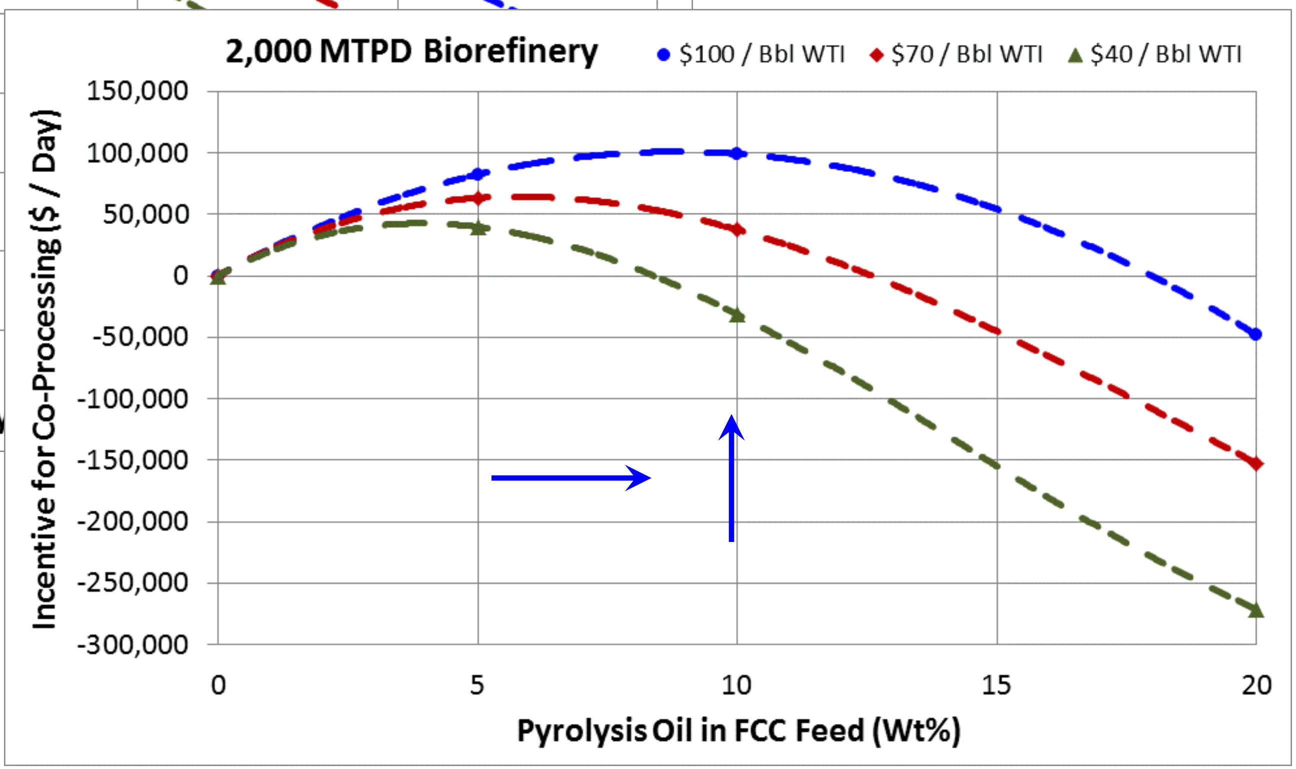


TEA Results – Pyrolysis Oil Co-Processing Value

"Why would anyone co-process more than 5 Wt%?"



FCC co-processing incentive
= $ / Volume x Volume

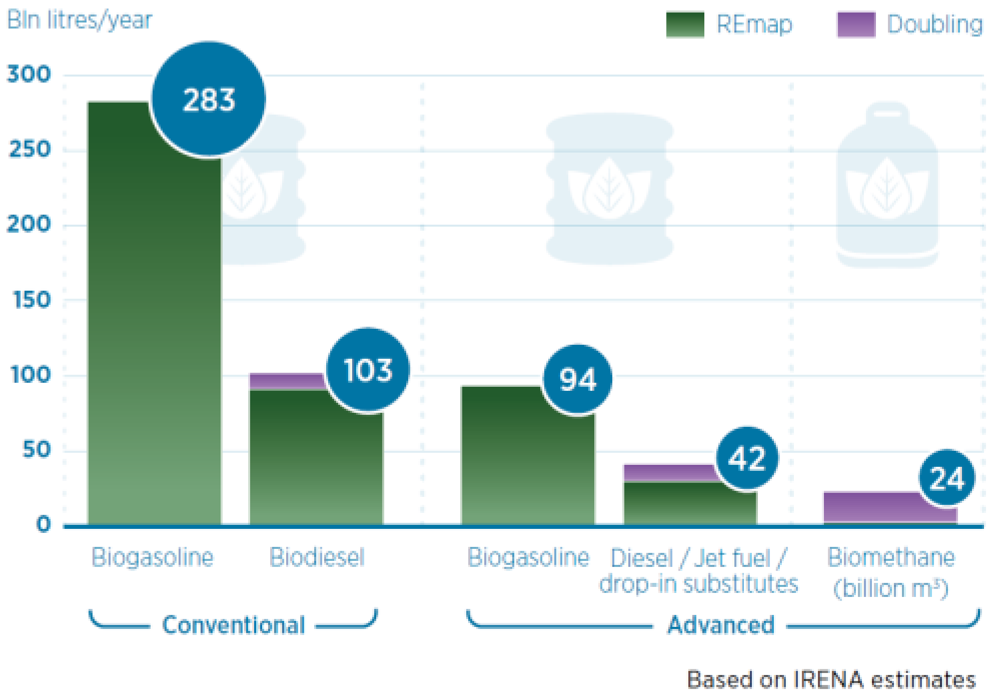


Technology improvements translate to increased co-processing incentives

Potential Impact of FCC Co-Processing

	United States	Global
FCC Processing Capacity (Bbl / Day)	6.0 Million	14.6 Million
Biofuels at 5 Wt% Pyrolysis Oil (B-GGE / Year)	1.0 – 2.8	2.4 – 6.8
Biofuels at 10 Wt% Pyrolysis Oil (B-GGE / Year)	2.0 – 4.4	4.9 – 10.7
Biofuels at 20 Wt% Pyrolysis Oil (B-GGE / Year)	5.0 – 6.3	12.1 – 15.2

IRENA Renewable Energy Roadmap 2016



Potential for **10+ Billion Gallons (GE) (40 B-Liters) biofuels per year** with 10% pyrolysis oil in FCCs.

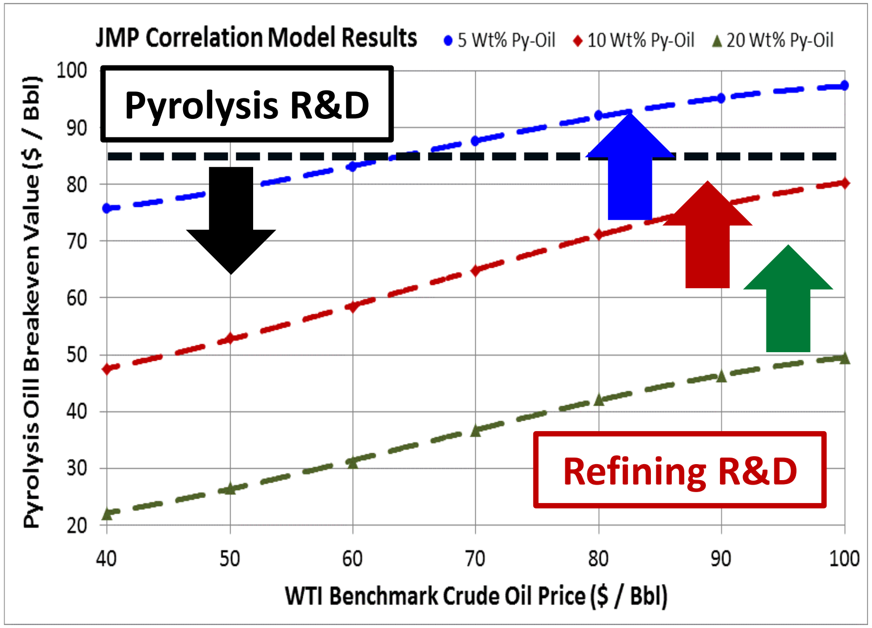
Conclusions and Next Steps for Analysis

Conclusions (based solely on NREL-Petrobras experiments, models and TEA)

- Co-processing up to 5% is economically feasible in near-term
- Co-processing up to 10% is economically feasible with progress in industry and technology
- Significant impact on TEA from lowering capital hurdle
- U.S. and global FCC capacities enable opportunity for substantial biofuels production

Next Steps

- Publish complete analysis results
- Pyrolysis R&D to reduce bio-oil cost
- Refining R&D to maximize value
    - FCC feed hydrotreating
    - Hydrocracking
    - Different bio-oils
    - Resid FCCs



Discussion on renewable product allocation methods for FCC co-processing for CARB Co-Processing Kick-Off Meeting (December 13, 2016)

Assessed Product Allocation Methods

Carbon-14 Analysis by ASTM D6866-16

Method based on C-14 results from NREL-Petrobras CRADA and additional data points from Petrobras literature using test method ASTM D6866-16. This method allocates mass of renewable carbon percent over total carbon (fossil and bio).

% Bio-Products = Bio-C by ASTM D6866 -16

Observed Yields from Co-Processing Experiments and JMP Model

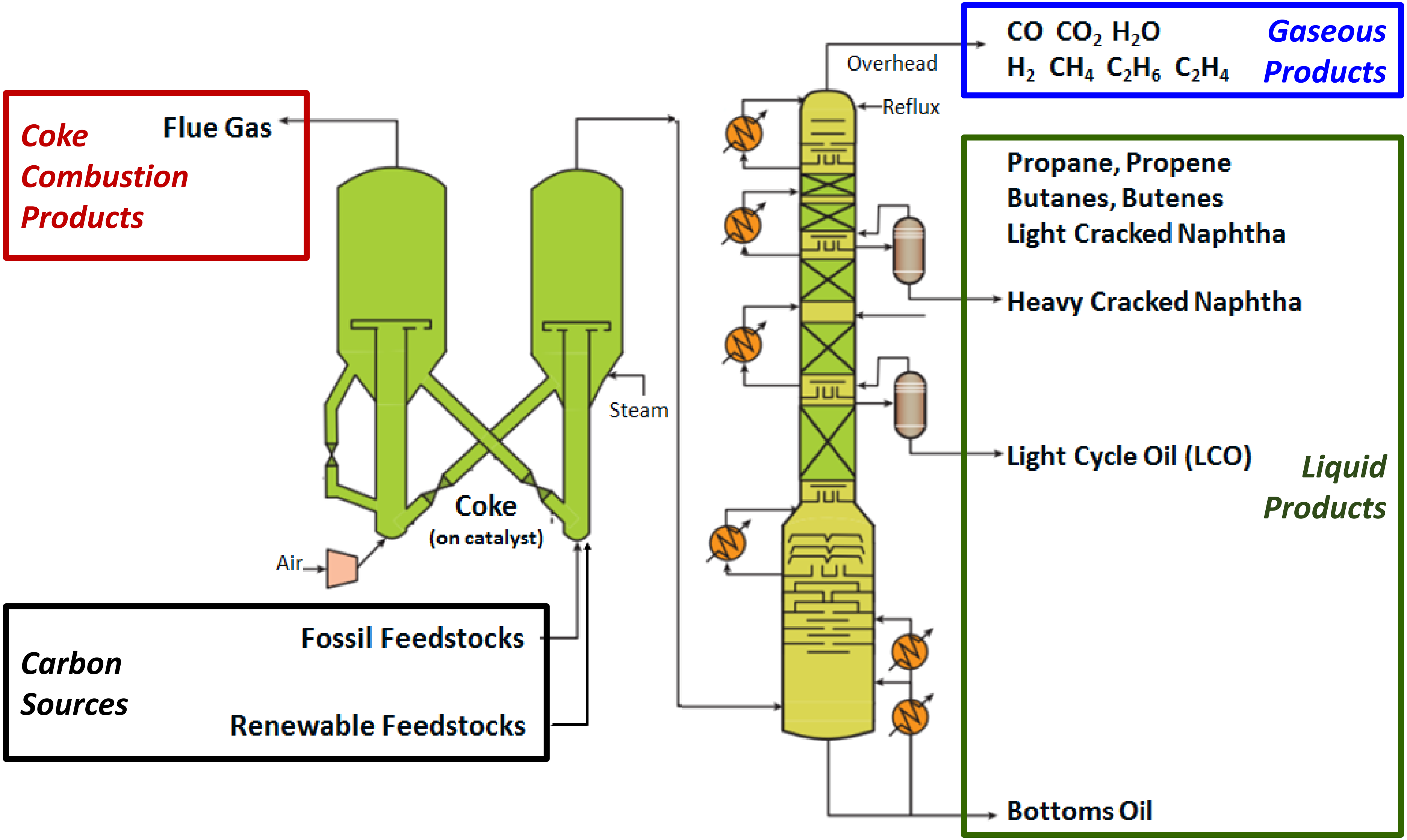
Method based on the observed yields from the experimental data assuming that the yields from VGO processing remain constant. In addition to the product-carbon from the pyrolysis oil, this method also allocates the VGO-carbon in products that were not present in VGO processing. For example, if a VGO-carbon yields coke for VGO processing and yields liquid product during pyrolysis oil co-processing, it is allocated as bio-carbon.

Py-Oil Liquid Product Yield = Overall Yield – (VGO-Only Yield * VGO%)

$$\%\ \text{Bio-Products} = \frac{\text{Py-Oil Liquid Product Yield}}{\text{Overall Liquid Product Yield}} * 100$$

Fluid Catalytic Cracking (FCC) Unit

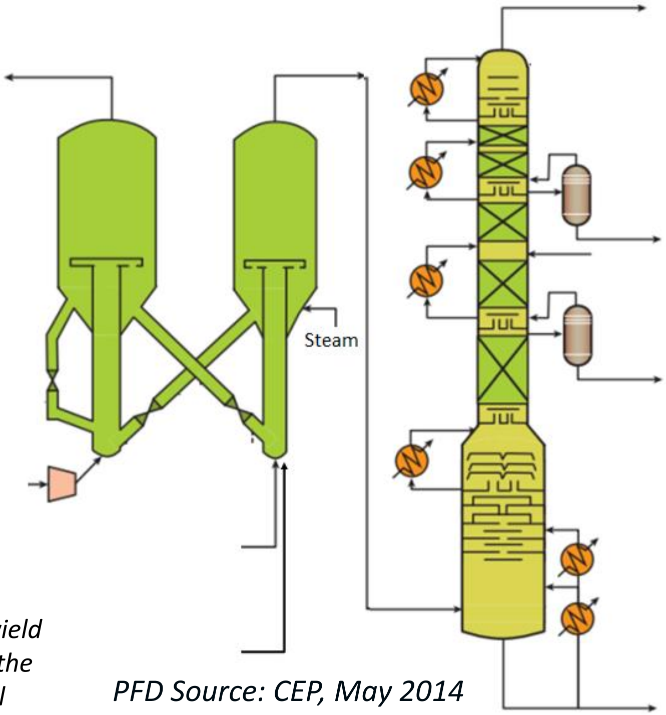
PFD Source: CEP, May 2014



C-Balance Example Based on Carbon-14

- Using C-14, VGO C-efficiency to liquid products increases with 5-wt% co-processing from 85.5% to 86.7%
- Py-oil gets c-efficiency credit of 32%
- Carbon-14 does not tell the whole story
- Carbon-14 may not account for full GHG reduction benefit

Carbon Sources		
	VGO Only	5-wt% CP
Fossil	1000	960
Bio		25
Total	1000	985



PFD Source: CEP, May 2014

Gaseous + Coke Products		
	VGO Only	5-wt% CP
Fossil	145	128
Bio		17
Total	145	145

Liquid Products		
	VGO Only	5-wt% CP
Fossil	855	832
Bio		8 *
Total	855	840

** Carbon-14 by ASTM D6866-16*

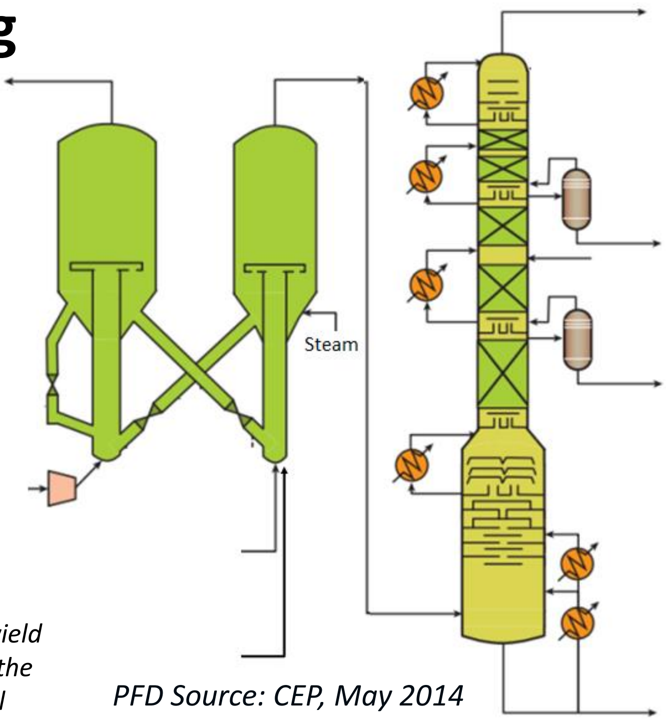
Note: Carbon balance examples represent rounded yield approximations from experiments and models from the NREL-Petrobras CRADA for illustrative purposes. Full analysis details are presented in in-progress manuscript.

C-Balance Example Relative to Base-VGO Yields

- **Calculates the overall observed impact of co-processing relative to base VGO-only yields (which would exist without co-processing)**
- **Captures full GHG reduction benefit and allocates to bio-oil**
- **C-efficiencies are: VGO 85.5% / Bio-Oil 76.0%**
- **Refiners have more incentive to pursue bio-oil co-processing**

Carbon Sources

	VGO Only	5-wt% CP
Fossil	1000	960
Bio		25
Total	1000	985



PFD Source: CEP, May 2014

Gaseous + Coke Products

	VGO Only	5-wt% CP
Fossil	145	139
Bio		6
Total	145	145

Liquid Products

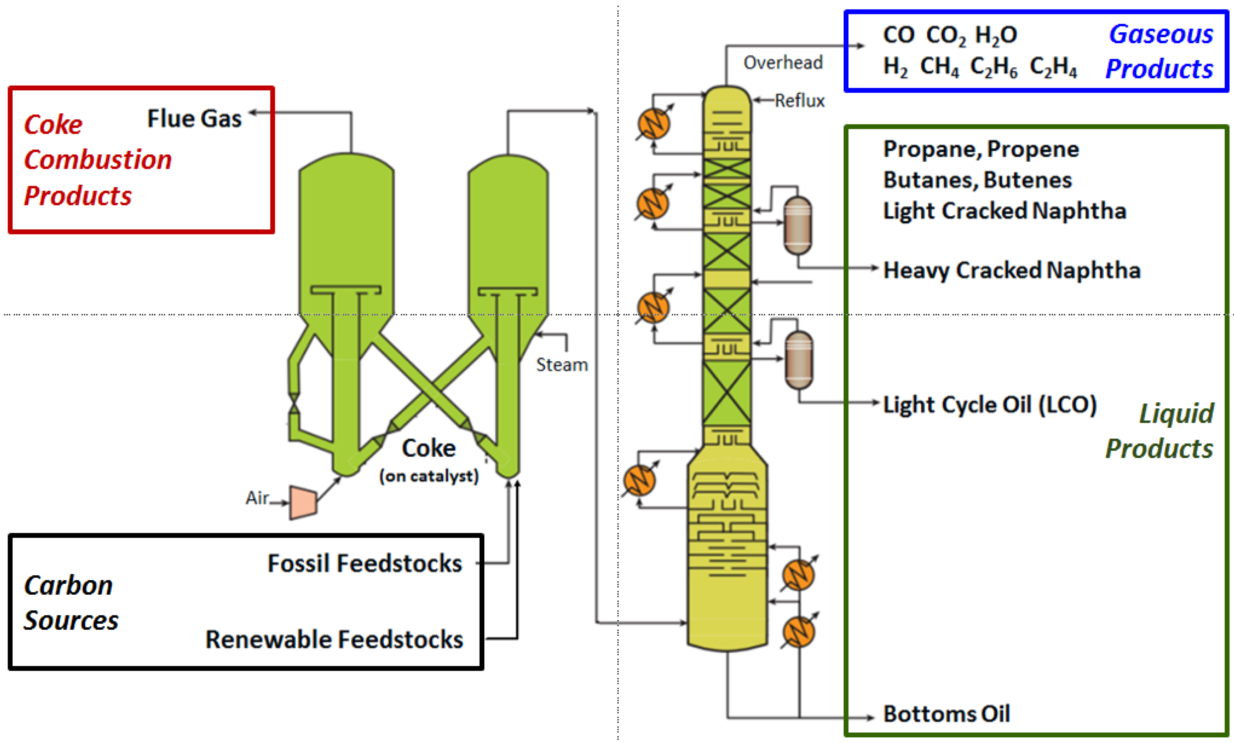
	VGO Only	5-wt% CP
Fossil	855	821**
Bio		19
Total	855	840

Note: Carbon balance examples represent rounded yield approximations from experiments and models from the NREL-Petrobras CRADA for illustrative purposes. Full analysis details are presented in in-progress manuscript.

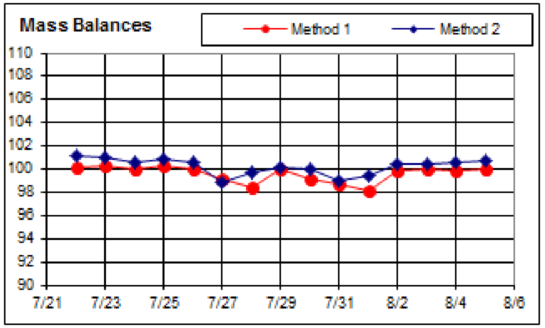
*** Set based on VGO-Only C-efficiency*

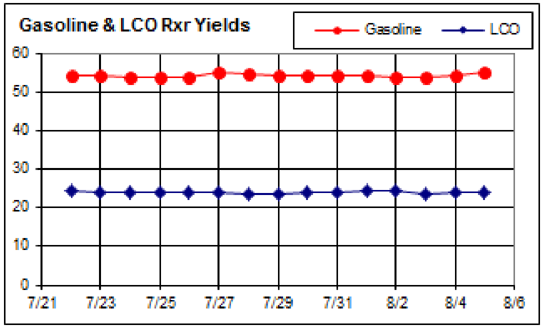
Mass Balance on FCC Unit

- Commercial FCC units are already equipped for yield method
- Flow rates measured and monitored continuously.
- Compositions / qualities are analyzed continuously or 2 x per day.
- Daily mass balance closures of ±2 % expected by management.
- Elemental balances often monitored as well.

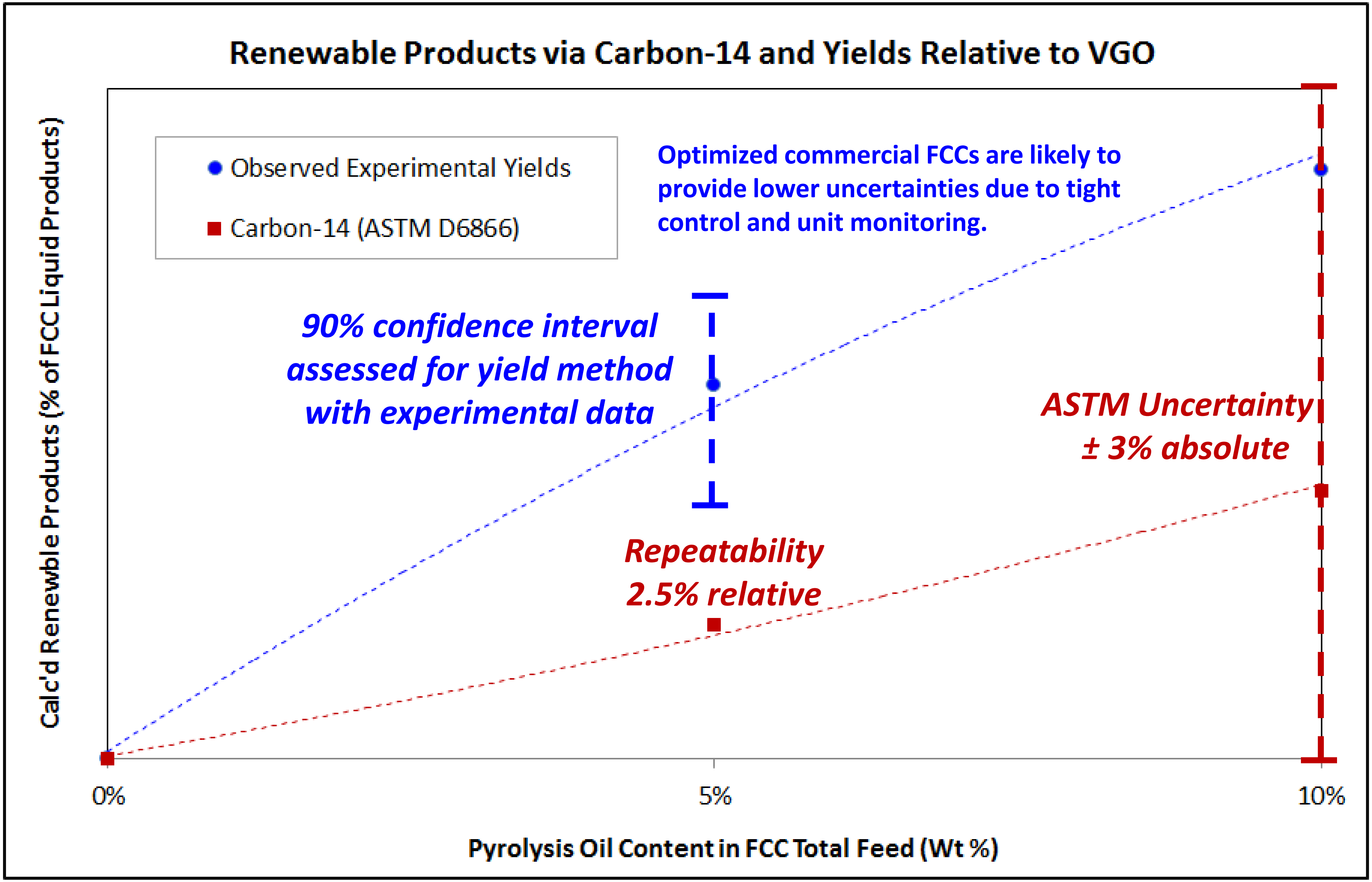


Examples of FCC Trends





Method Results and Uncertainties



Summary

DRAFT

NREL and Petrobras have extensive FCC co-processing experience using Ensyn's bio-oils

- NREL experience in high precision renewable diesel and gasoline analysis from coprocessing bio-oil (Beta Analytic ASTM D6866-16 method B) indicates:
  - Bio-oil in diesel is detected with high repeatability because the SwRI base fuel included biodiesel in the base blendstock.
    ^{14}C = Renewable carbon is present qualitatively!
  - Bio-oil in gasoline is detected as a very small signal with good repeatability.
  - ASTM uncertainty: **^{14}C % ± 3% (absolute)** - inherent
  - Qualitative methodology unless samples with **^{14}C >5% renewable C over total C**
- NREL concludes on yields of renewable gasoline and diesel from FCC co-processing:
  - Mass balance procedures are accurate, reliable and appropriate to determine renewable gasoline and diesel yields attributable to the addition of bio-oil in FCC co-processing operations, particularly for bio-oil addition under 10%.
  - **^{14}C** is not an accurate or reliable method to determine renewable finished gasoline and diesel yields attributable to the addition of <10 wt.% of bio-oil in FCC co-processing.

These results of the Petrobras/NREL CRADA are being written up for submission in peer-reviewed publications.

Compounded uncertainty of ^{14}C AMS measurements [1]

AMS=Accelerated Mass Spectrometry

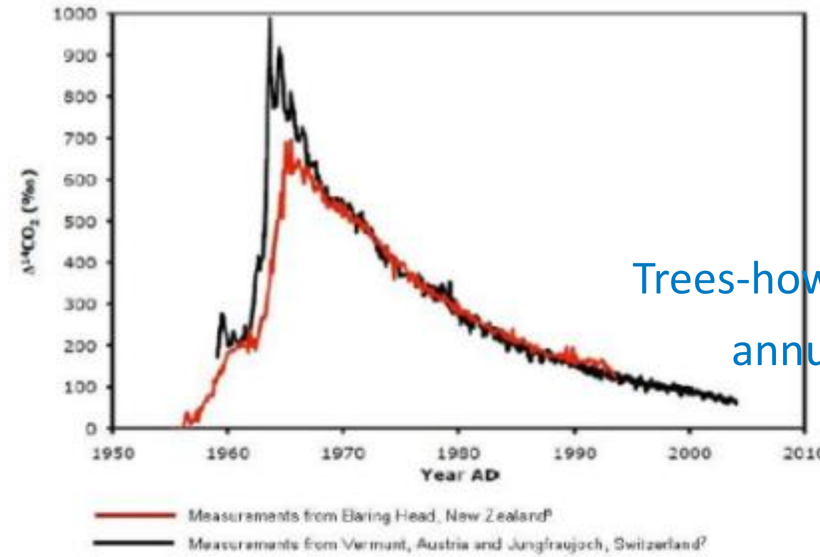
AMS ^{14}C measurement compares the $^{14}C/^{12}C$ ratio of an unknown sample to that of a known standard, expressed in percent Modern Carbon (pMC).

The raw data, the ^{14}C counting rate and ^{12}C (or ^{13}C) current of the unknown undergo several calculation steps, each with its own uncertainty:

- a comparison to the $^{14}C/^{12}C$ ratio of a known standard,
- an isotopic fractionation correction,
- a machine background subtraction,
- a process blank subtraction.

Percent Biogenic Carbon= pMC divided by 101.5 (ACF)

Atmospheric Correction Factor (ACF) one more source of uncertainty [2]



Trees-how old? annuals

TABLE 1 Percent Modern Carbon (pMC) Reference

Year	REF (pMC)
2015	102.0
2016	101.5
2017	101.0
2018	100.5
2019	100.0
2020	to be determined

Coprocessing produces low ^{14}C content samples [3]!
Biobased products have much higher contents [2]

[1] Nadeau & Grootes, " Calculation of the compounded uncertainty of ^{14}C AMS measurements", Nuclear Instruments & Methods in Physics Research B 294 (2013) 420–425.

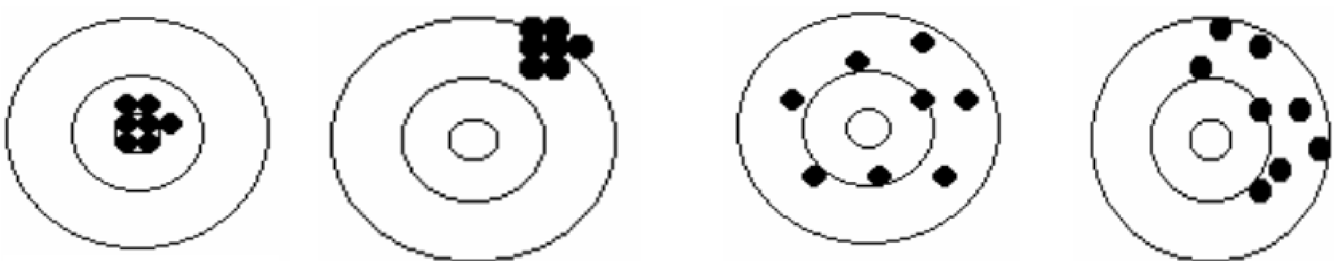
[2] Ramani Narayan, http://www.soybiobased.org/assets/content/documents/Narayan_Presentation_ASTM_D6866-16.pdf

[3] Pinho, A.R., de Almeida, M.B.B., Mendes, F.L., Casavechia, L.C., Talmadge, M.S., Kinchin, C., Chum, H.L. "Fast pyrolysis oil co-processing from pinewood chips with vacuum gas oil in an FCC unit for second generation fuel production," Fuel, 188 (2017) 462-473. Open access at http://dx.doi.org/10.1016/j.fuel.2016.10.032

Differences between Accuracy and Precision

- **Accuracy** is the closeness of agreement between a measurement and the true or reference value. If we imagine a series of measurements, each with the same true value, then if the average of the measurements does not equal (within error) the true value, then the measurement is said to be biased, where the bias is the difference between the **expected value** or average of a large series of measurements and the true value. Bias is usually considered to be a systematic error.
- **Precision** is the closeness of agreement between a series of independent measurements obtained under identical conditions. Precision depends on the **distribution of random errors**, and is commonly computed as the standard deviation of the results. As the standard deviation increases, the precision decreases (RSC 2003a,b).

The archery targets in Figure 4 below depict accuracy and precision graphically.



Accurate and precise | Inaccurate and precise | Accurate and imprecise | Inaccurate and imprecise

Repeatability (*r*) refers to measurements made under identical conditions in 1 laboratory, while reproducibility (*R*) refers to measurements made in different laboratories, under different conditions. Both repeatability and reproducibility are the closeness of agreement between the ^{14}C ages under these 2 different scenarios. The reproducibility standard deviation quantifies the maximum variability in results.

Scott, E.M. et al., ERROR AND UNCERTAINTY IN RADIOCARBON MEASUREMENTS, Proceedings of the 19th International 14C Conference, edited by C Bronk Ramsey and TFG Higham RADIOCARBON, Vol 49, Nr 2, 2007, p 427–440

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Biobased and Biogenic Carbon Testing Laboratory

ISO/IEC 17025:2005 Accredited

Report of % Biogenic Carbon Content Analysis: ASTM D6866-16 Method B(AMS)

Explanation of Results

ASTM D6866-16 cites the definition of biogenic as containing carbon (organic and inorganic) of renewable origin like agricultural, plant, animal, fungi, microorganisms, macro-organisms, marine, or forestry materials. "Renewable" is defined as being readily replaced and of non-fossil origin, specifically not of petroleum origin. Therefore, % biogenic carbon testing results most commonly indicate the amount of non fossil derived carbon present. It is calculated and reported as the percentage renewable carbon present relative to total carbon (TC) present.

Two methods of analysis are described in ASTM D6866-16 - Method B (AMS) and Method C (Liquid Scintillation Counting (LSC). Method B is the most accurate and precise and was used to produce this result. The methods determine % biogenic carbon content using radiocarbon (aka C14, carbon-14, 14C). The C14 signature is obtained relative to modern references. If the signature is the same as CO2 in the air today, the material is 100 % biogenic carbon, indicating all the carbon is from renewable sources and no petrochemical or other fossil carbon is present. If the signature is zero, the product is 0 % biogenic carbon and contains only petrochemical or other fossil carbon. Values between 0% and 100% indicate a mixture of renewable and fossil carbon.

The analytical term for the C14 signature is percent modern carbon (pMC) and will typically have a cited error of 0.1 – 0.4 pMC (1 RSD) using Method B. Percent modern carbon is the direct measure of the product's C14 signature to the C14 signature of modern references. The modern reference used was NIST-4990C with a C14 signature approximating CO2 in the air in AD 1950. AD 1950 is chosen due to the "BOMB CARBON EFFECT". This effect is a consequence of atmospheric thermonuclear weapons testing between 1952 and 1963. During this period, the 14CO2 content in the air increased by 90%. This means that a plant living in 1963 would measure about 190 pMC. Since the signing of a test ban treaty in 1963, this signature declined to about 140 pMC by 1975, 120 pMC by 1985, and 102 pMC by 2015. For example, to obtain the % biogenic carbon content of a product relative to living biomass in 2015, the pMC value needs to be divided by 1.02. ASTM D6866-16 cites a constant decline in this value of 0.5 pMC per year and provides requisite values to be used according to the year of measurement. The adjustment factor is termed "REF".

The consequence of bomb carbon is that the accuracy of the % biogenic carbon content will depend on how well REF relates to when the biogenic material in the product was last part of a respiring or metabolizing system. The most accurate results will be derived using biogenic material from short-lived material of very recent death such as corn stover, switch grass, sugar cane bagasse, coconut husks, flowers, bushes, branches, leaves, etc. Accuracy is reduced in materials made from wood contained within tree rings. The rings within trees each represent the previous growth season with the previous year's 14CO2 signature. The center most ring of a tree living today but planted in 1963 would be about 190 pMC whereas the outermost ring/bark would be the present-day air pMC (e.g. 102 in 2015). If this tree is harvested and used in manufacturing a biogenic product, the % biogenic carbon of the product will depend on where the carbon came from within the tree. ASTM D6866-16 cites to use average values of past carbon pMC for REF when values greater than 100 pMC are measured. For more details, the Standard can be purchased from the ASTM International website (www.astm.org).

ASTM D6866-16 also cites requirements for materials of known aquatic origin and options for analyzing materials for which a single C14 measurement cannot produce a % biogenic carbon content value (complex products). Also, reporting requirements are cited.

The result provided in this report is unique to the analyzed material and is reported using the labeling provided with the sample. Although analytical precision is typically 0.1 to 0.4 pMC, ASTM D6866 cites an uncertainty of +/- 3 % (absolute) on each % biogenic carbon result. The reported % biogenic carbon only relates to carbon source, not mass source.

uncertainty

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